

REACTIONS AT THE TEMPERATURE OF THE ELECTRIC ARC.

A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIRE-
MENTS FOR THE DEGREE OF DOCTOR OF PHILOS-
OPHY IN THE FACULTY OF PURE SCIENCE
OF COLUMBIA UNIVERSITY.

BY

Herbert Raymond Moody, S.B., A.M.

EASTON, PA. :
THE CHEMICAL PUBLISHING COMPANY.
1901.

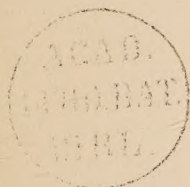
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ACKNOWLEDGMENT.

For their kindness and cooperation, the author wishes to express his thanks to the entire instructing staff of the chemical department.

Particularly are thanks rendered to Doctor Chandler and Professor Pellew for the advice which they have offered and the interest they have uniformly manifested.

To Mr. Samuel Auchmuty Tucker, deep indebtedness is felt. His interest throughout the entire work, his advice, and his expenditure of time as a co-worker, have done much towards the attainment of what success has been reached.

H. R. M.

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Reactions at the Temperature of the Electric Arc.

The subject-matter of this work may, with convenience, be divided into four sections.

1st. An attempt to produce a source of either ethyl or methyl compounds from elementary carbon and cheap inorganic substances and, in connection with this, some experiments on the reducing powers of decomposing carbides.

2nd. An investigation of the possibilities of "fixing" atmospheric nitrogen to electric furnace products in such a way that ammonia would be the result of subsequent decomposing action.

3rd. A study of the reduction of phosphates, leading to the possibility of making phosphides without first making elementary phosphorus.

4th. The formation of some hitherto unknown borides of the metallic elements.

Incident to the main work, considerable time was devoted to the perfection of a convenient form of electric furnace and also to the proper method of analyzing a mixed gas composed of acetylene and ethylene.

The vertical (or crucible) form of electric furnace as perfected by Mr. S. A. Tucker¹ was not entirely convenient for this work, and anyone who has used a Moissan type furnace of chalk or quick-lime knows that they are far from being desirable. Consequently the type of horizontal furnace as shown in the reproduced photograph in Plate I and in the outline drawing Plate II was designed, and proved to be eminently satisfactory.

Carbon bricks, 12 inches by 4 inches by 2 inches were used. These were luted together with a mixture of 75 per cent. powdered fire-clay and 25 per cent. powdered graphite. Pastes composed respectively of 10, 20, 30, and 40 per cent.

¹ Am. Electrician, Vol. XI, Sept. '99, p. 408.

fire-clay were tried and found to be worthless. Eighty per cent. of clay was also tried and this, too, was a poor proportion. Subsequently, a "stove-paste" prepared for the trade was substituted and this proved to be more convenient and fully as efficient.

The sides of the furnace were of 6-inch bricks, thus making a working space of about 6 by 4 by 2 inches. This space could, of course, be increased or diminished at will for varying bulk of charges. The whole was then clamped and held firmly together by iron cross-bars provided with adjusting screws at each end. These bars are insulated from the furnace by strips of thick asbestos.

The end bricks were perforated with 1.5-inch holes containing a collar of asbestos or a small cylinder of clay. Through such collars the carbon electrodes (1 inch by 12 inches) passed into the furnace chamber.

Connection was made with these electrodes by copper "sleeves" lined with copper gauze and tightened with set-screws which at the same time carried copper lugs that held the leading cables.

The tendency to overheat those portions of these electrodes outside of the furnace, and the consequent wasting away, and also the tendency to melt the copper connections, were overcome by either one of two expedients; that is, either by the use of the water-jacket as shown in Plate I, or by heavily copper plating the carbons. This latter did not furnish quite as perfect a protection, but it was somewhat less troublesome than the former and was consequently the one most used.

This furnace has the advantage of protecting the operator from the disagreeable strong light and heat which are such a disadvantage in the crucible type and of preventing largely the loss by ascending gas currents of any of a light-weight charge. It also avoids the introduction of silica which usually happens when a fire-brick furnace is used. Most important of all such a furnace is durable. Only three sets of bricks were used throughout the year in which nearly a hundred runs were made. Oftentimes, ten or twelve runs could be made without dismantling the principal parts and the

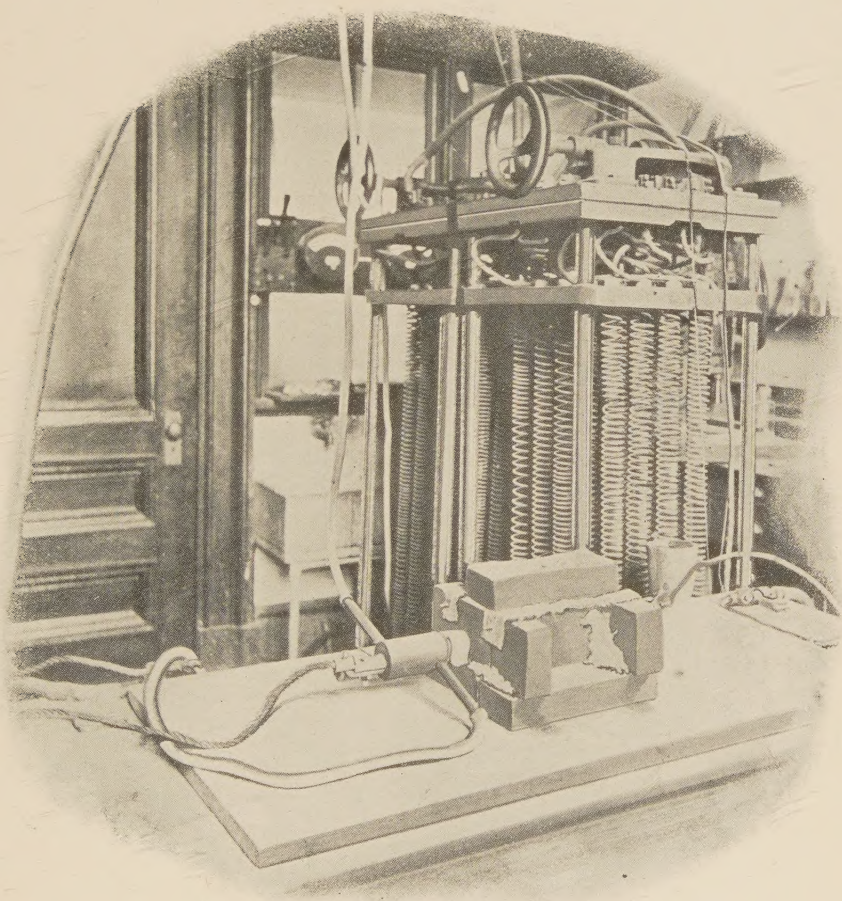


PLATE I.

substitution of new asbestos collars served to make everything ready for the next run. These advantages are most apparent to those who have been obliged to saw out a new chalk furnace for nearly every run.

In this type of furnace the desired current may be easily maintained throughout the entire fusion and this is not easily done with a crucible furnace where variations are unknowingly introduced by the constantly changing distance between the poles.

In connection with the foregoing type, a double arc furnace was constructed in the same general form as shown in Plate II only having two sets of carbons arranged in series.

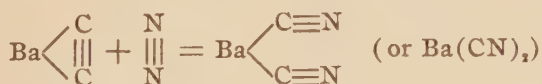
Interesting figures in economy were obtained by using this. For example, with the single arc furnace having a polar separation of 18 millimeters and enough resistance in circuit, the following reading was obtained: 125 amperes, 70 volts and consequently 8,750 watts. These should be compared with the following obtained while using the double arc furnace. Here all the external resistance was cut out and then the instruments showed 150 amperes and 90 volts. A few moments after this the reading was 125 amperes and 100 volts, or 12,500 watts.

The foregoing figures show, of course, a far greater economy, when a 110 volt current is used, since the heating effect is proportionate to the number of watts and none of the current was used up by introducing outside resistance.

The only difficulty in using this type is to prevent the extinction of the arcs, but that trouble is far from insurmountable.

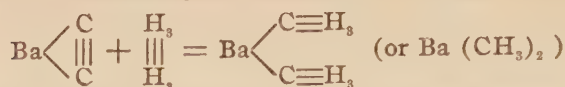
PART I.

The metallic compounds of methyl are, of course, well known and since barium carbide is an unsaturated compound, it was thought possible that a barium methyl might be produced just as barium cyanide is now formed.¹



¹ C. B. Jacobs, U. S. Patent No. 657,937.

That is, it seemed possible that the following might occur.



The instability of this class of compounds argued against the reaction, but it seemed worth trying as a successful result meant a new inorganic source of methyl compounds.

Consequently, runs one to eight, inclusive, were made with the purpose of discovering the best conditions for producing a porous product, and at the same time a substance which should contain a fair amount of carbide. For this work witherite and coarsely ground coke were used. The witherite, on analysis, showed a content of iron, aluminium, barium, calcium and silica in the following proportions :

	Per cent.
BaCO ₃	92.06
CaCO ₃	1.3
Al ₂ O ₃ and Fe ₂ O ₃	1.7
SiO ₂	4.9
	99.96

Moissan¹ gives as the proper proportions for making barium carbide, barium carbonate 150 grams, coke 25 grams.

In Run I, in order to produce porosity, more carbon than this was used, that is, barium carbonate 300 grams, coke 60 grams. With 200 amperes and 50 volts for ten minutes, a product was obtained 2 grams of which, when treated with water, yielded 35 cc. of gas.

Thirty-five cc. of acetylene weigh 0.04118205 gram and the theoretical weight of gas which should be evolved from 2 grams of barium carbide is 0.32 gram, so this product yielded only 13 per cent. of the theoretical amount of gas.

In Run II, 75 grams of coke were used and the same amount of heat. Two grams of this product yielded 36.4 cc. of gas, but was found to be not essentially more porous.

In Run III, the charge consisted, as in Run I, of 300 grams of barium carbonate and 60 grams of coke; the amperage was

¹ Le Four Électrique, p. 301.

cut down to 150, the voltage to 40 and this current maintained for fifteen minutes. Two grams of this product yielded 50 cc. of gas.

In Run IV, a large excess of coke was tried using 60 grams to 150 of barium carbonate. The amperage was kept at 160 and the voltage at 50; time, twenty minutes. This product was more granular but of low grade as is shown by 2 grams of it yielding only 25 cc. of gas.

In Run V, the charge consisted of 300 grams of barium carbonate with 60 grams of coke. Amperes, 165; volts, 50; time, twenty minutes. This product was also poor as two grams of it yielded only 25 cc. of gas.

In Run VI, the proportions were 300 grams of barium carbonate to 40 grams of coke. Amperes, 160; volts, 70; time, ten minutes. The charge was added in small successive portions and 0.75 gram of the product gave 42 cc. of gas.

In Run VII, the advantage of using barium oxide instead of barium carbonate was tried. The charge was made up of 150 grams of barium oxide and 25 grams of coke. The current used measured 160 amperes and 50 volts and it was maintained for six minutes. A sample of this product weighing 0.75 gram yielded 44.2 cc. of acetylene thus showing a little improvement over Run VI.

In Run VIII, a return was made to barium carbonate and the charge was composed of 300 grams of witherite and 50 grams of coke. Amperes, 150; time, twelve minutes. Seventy-five one-hundredths of a gram of this product yielded 95.2 cc. of gas which compares favorably with the amount obtained from a commercial sample of barium carbide. Consequently in subsequent work the general conditions of Run VIII were observed.

The apparatus used for measuring the gas evolved from the preceding samples was quite simple, and, as it made little difference whether or not heating and consequent polymerization¹ took place, in this and in similar work it answered very well. Of course, owing to the fact that but little dilute acid was

¹ Lewes, "Acetylene," p. 102.

used for each evolution, change due to heating was almost certain to take place. But this, after the gas had assumed room temperature, would make little difference in the volume.

The apparatus is shown in Plate IV, and it consisted of a pair of ordinary Hempel burettes filled with mercury and connected to the evolution flask and also to the burette containing the dilute acid. Opening pinch-cocks B and D after the carbide was placed in A, and then raising F, caused the capillaries and A to become completely filled with mercury; then closing B, and lowering F (with C closed, of course), caused A to empty. Then if C were opened and a few cubic centimeters of dilute acid were thus admitted, evolution of gas commenced and could be collected unimixed with any air in E and A. Then by connecting a third burette at B, and opening the cock and raising F, E and A again became filled with mercury and the volume was read off in the third burette.

In Run IX, an attempt was made to produce barium methyl by the addition of hydrogen to barium carbide which had not yet become cool.

A porous carbide was desired, so the figures determined by Run VIII were used; *i. e.*, witherite 300 grams, coke 50 grams. The run was for twelve minutes, using 150 amperes and 60 volts.

One of the carbon electrodes had been cored with a one-sixteenth-inch hole, passing from end to end. In the outer end of this hole a small brass tube was inserted and luted tight with plaster of Paris. This was then connected to a Kipp hydrogen generator. The gas from the generator was first washed and then dried with calcium chloride.

As soon as the current was shut off, the hydrogen was admitted and all the outlets of the furnace were covered; the gas was passed in for five minutes. The product thus produced was reddish on fracture; it did not evolve gas rapidly from water, but was eventually entirely disintegrated.

To see if any liquids resulted from the water decomposition, 80 grams of the product were placed in 250 cc. of water and heated for an hour, the steam being passed into a return condenser.

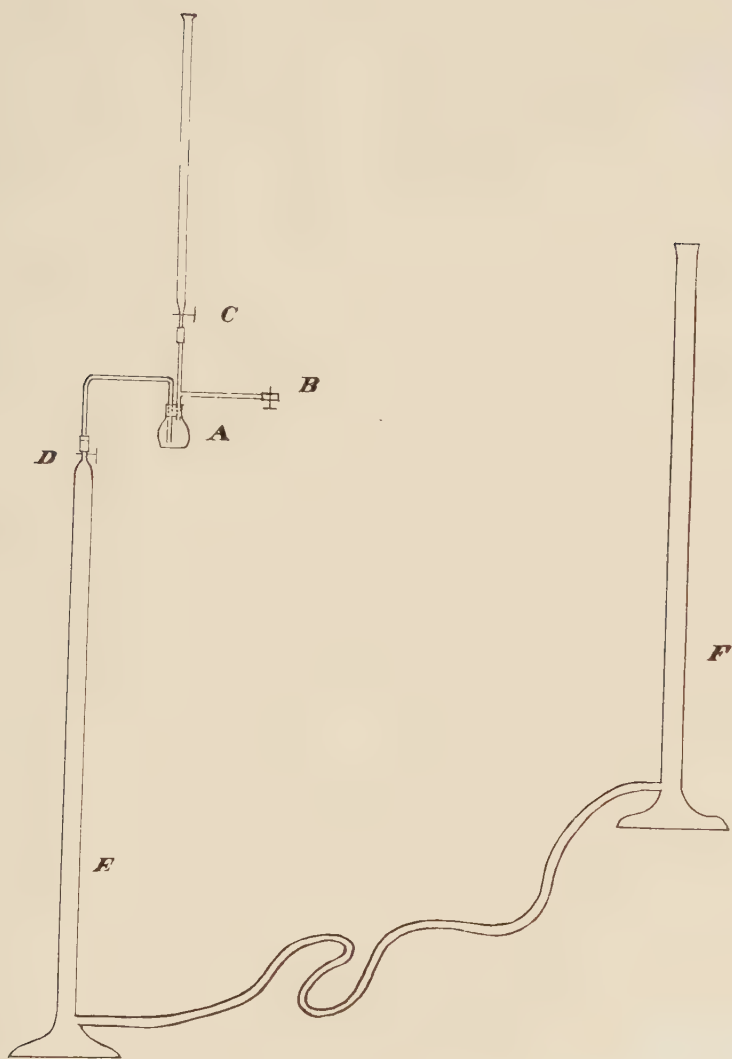


PLATE III.

On cooling, the flask was found to be filled with a white solid. The filtrate from this was pale straw color and, after removing the barium from it by dilute sulphuric acid, its boiling-point was found to be 100° C, showing it to be nothing but water. The white solid, on treatment, proved to be nothing but barium hydrate. So here there had been no tendency to produce any addition-product.

In Run X, a similar charge and current were used but, after the first seven minutes had passed, the hydrogen was introduced and continued through the subsequent five minutes of the run and also for five minutes after the current was shut off. This product did not differ from that obtained in Run IX.

In Run XI, similar charge and current were used, but in this case the hydrogen was admitted simultaneously with the turning on of the current for five minutes after the switches were opened. This product evolved gas freely from warm water and the result was the same as in No. 10, as only barium hydrate and a filtrate which proved to be nothing but water, were produced.

At this point it seemed desirable to analyze the gas evolved from this product and it was here that the apparatus shown in Plate IV was found to be unsuitable for generating gas for *analysis*. By subsequent analysis, the gas evolved from No. 11 was shown to be all acetylene, while by using this apparatus 9.5 cc. out of 100 cc. were apparently not acetylene.

It was thought for some time that this residue was all air which had leaked in around the stopper of A and, to prevent this, the whole flask was immersed in mercury. But even with this precaution some residue still remained from the ammoniacal cuprous chloride which was used as the acetylene absorbent. Similar results were obtained when commercial barium and calcium carbides were used showing that the residue was only in part air. This also proved that the residual gas was not the result of adding hydrogen to the carbide.

Consequently another form of apparatus was devised which is shown in Plate V.

In this all the joints were mercury sealed and the air was exhausted with a Boltwood pump. Then the dilute hydrochloric acid was introduced from the attached burette as had been done in the former apparatus. The gas thus evolved passed directly into the top of the working tube of an Elliott apparatus.

Although by using this apparatus there was not the slightest evidence of any air contamination, yet the process was open to the same objection as the former one; that is, the formation of other gases than acetylene owing to the high temperature of evolution. For example, the barometer stood at 760 mm. and so did the manometer on the pump. Under these conditions a sample of gas measuring 100 cc. was taken which left a residue from ammoniacal cuprous chloride that measured 2.3 cc. This residue underwent no absorption either by caustic potash or alkaline pyrogallate solution proving it contained neither oxygen nor carbon dioxide. So the residue could not have been unintentionally introduced air, but was a gas formed by a change in the acetylene.

Consequently in all subsequent work a very simple, convenient and rapid working apparatus was used. This is shown in Plate VI. It consisted of an ordinary test-tube attached by a capillary and connector to the three-way cock of the working tube of the Elliott apparatus. The test-tube was filled even full of the liquid (water, dilute acid, etc.) from which the evolution was to be made and, as there was considerable bulk, it usually stayed cool and, if not, it could be immersed in water or ice.

To lessen the volume of acetylene absorbed, the two burettes were filled with a saturated solution of sodium chloride.¹

The method of use was as follows: The lower and connecting cocks being opened the leveling bottle of the measuring tube is raised causing brine to fill the capillary. Then the sample is dropped into the test-tube and the stopper, already attached to the capillary, is thrust quickly into place. Thus the evolved gas is caused to rise through the working tube and over into the measuring tube, from whence, when a suf-

¹ Lewes, "Acetylene," p. 66.

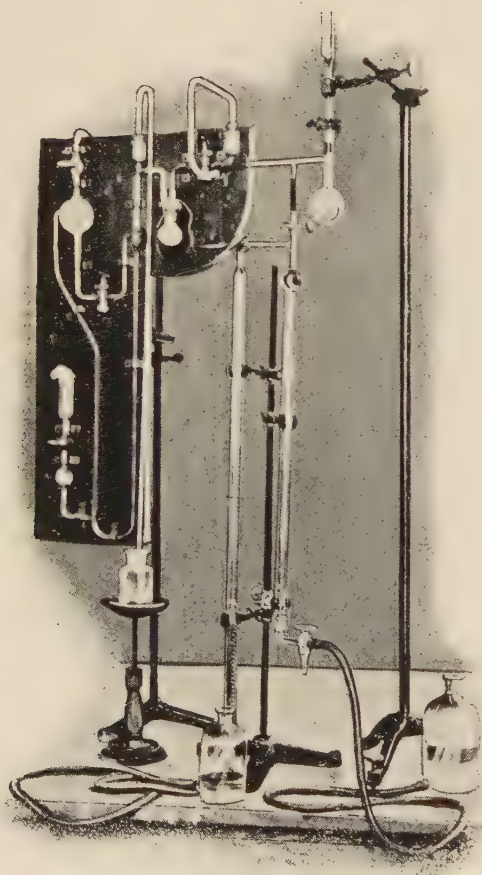


PLATE IV.

ficient volume has been generated, it may be returned to the working tube for analysis.

In Run XII, a return to the original investigation was made. Similar charge, current, and time were employed with a variation in the introduction of the hydrogen, that is, instead of introducing the gas through the electrode, thus causing it to pass over the charge, it was passed in through the roof of the furnace through a carbon tube. The lower end of this tube dipped into the charge and caused the gas to pass through the carbide.

Both hydrogen and current were simultaneously turned on and the gas, after the current was stopped, was allowed to pass for five more minutes. The gas evolved from this product showed on analysis that it was all acetylene, therefore no positive results were obtained.

In Run XIII, a distinct change in the proportions of the charge were made, using equal portions of witherite and coke (175 grams). One hundred and fifty amperes were used, with the low voltage of 30. The hydrogen was turned on simultaneously with the current and continued for five minutes afterward.

The product, looking like agglomerated coke, was porous, but it evolved gas freely from water showing that some carbide had formed. Fifty grams of it were boiled using a return condenser, and the filtrate, when freed from barium, had a boiling-point of 100°C . showing it to be all water.

These five runs (9-13) seemed to exhaust the different condition which might be applied to forming barium methyl and as no signs of such a compound having been formed had been noticed, the idea was abandoned.

In the next set of runs the fundamental idea was to produce such a combination of carbide of aluminium and carbide of calcium, that when the product was acted upon by water there might result, either directly or by interaction, a different gas than is produced by either of them taken alone. It was thought probable that ethylene might be so formed.

As every one knows simple calcium carbide reacts with water as follows¹:



The carbide of aluminium, however, decomposes water differently and causes the following reaction²:

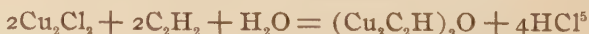


Knowing this, it seemed possible that the acetylene and the methane in the nascent state might react, or that the mixed carbides would form a combination which would decompose with water giving some such gas as ethylene.

Before anything was done towards making this mixed product it was necessary to be sure regarding a method of separating mixed acetylene and ethylene, for even if the desired reaction took place, there would undoubtedly be some acetylene to be absorbed.

The usual solvent recommended for acetylene is ammoniacal cuprous chloride.³ This solution is made up of 42 grams of cupric chloride, 32 grams of copper turnings, 100 cc. of hot water and 200 cc. of commercial hydrochloric acid. This mixture is boiled two or three hours and then a little concentrated hydrochloric acid is added and the whole boiled till it is pale yellow. This was cooled and an excess of ammonium hydrate added.⁴

Such a solution was found to absorb pure acetylene rapidly and completely by the following reaction:



The next step was to investigate the solubility of known ethylene. This gas was generated by the action of metallic zinc on ethylene di-bromide.



Ethylene is so little soluble in water, one volume of water absorbing at t°:

¹ Moissan, "Le Four Électrique," p. 296.

² Moissan, "Le Four Électrique," p. 325.

³ Hempel, "Gas Analysis," p. 183.

⁴ Vulté and Neustadt, "Inorganic Preparations," p. 73.

⁵ Hempel, "Gas Analysis," p. 183.

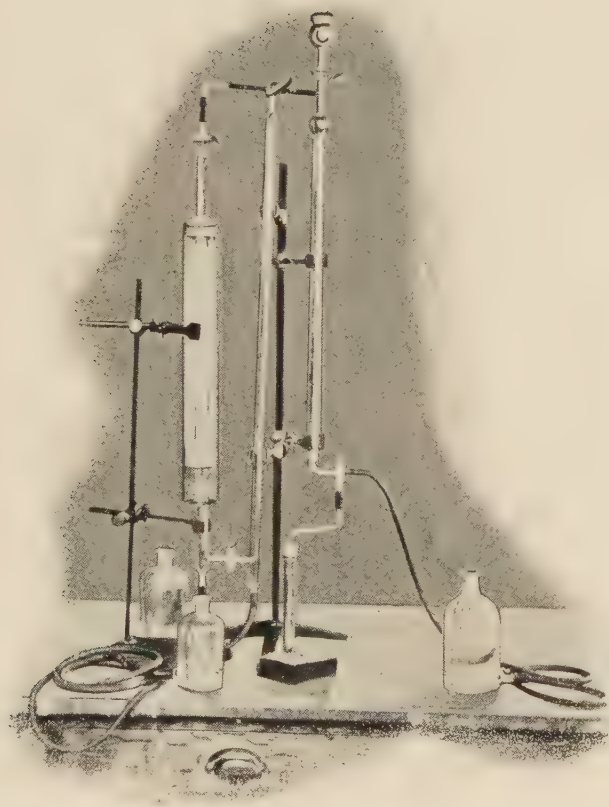


PLATE V.

$0.25629 - 0.0091363.t + 0.000188108.t^2$ volumes of ethylene,¹ that there was no trouble to apprehend from such a small amount being absorbed. This was proved by actual trial, as was also the solubility in ammonium hydrate. Here again very slight solubility was noticed.

Considering these two facts and the fact that ethylene is not usually considered to be soluble in cuprous chloride, it seemed surprising, when either ammoniacal or acid cuprous chloride was added to a sample of ethylene, to find that fully 95 per cent. of the gas was absorbed.

This result was found to be substantiated by Hempel on page 161 of his "Gas Analysis." Here it is stated:—"solutions of cuprous chloride are absorbents not only for carbon monoxide and acetylene, but also for ethylene, a fact not taken in to account in a number of gas analyses lately published." As stated above, results obtained here tallied almost exactly with those of Hempel.

The foregoing is apparently not taken into account by Moissan, whose results, according to the method of procedure given on pages 313 and 320 of "*Le Four Électrique*," can hardly be right. To be sure, the method is spoken of only in a vague way, but as stated in the references given, it is natural to suppose that ethylene was considered as insoluble in the copper salt. If this were the fact, a large portion of the ethylene evolved from his thorium carbide must have been absorbed with the acetylene and counted with the latter.

Thinking that a mixture of acetylene and ethylene might act differently from either taken alone, equal volumes of the two gases were mixed and nearly the total volume was found to be absorbed by the copper solution.

Other good solvents of acetylene are alcohol (one volume of alcohol dissolves 6 volumes of acetylene)² and acetone (one volume of acetone dissolves 25 volumes of acetylene).³

To investigate the possibilities of using either of these to absorb the acetylene and leave the ethylene, the solubility of

¹ Beilstein, Vol. I, p. 112.

² Lewes, "Acetylene," p. 66.

³ Lewes, "Acetylene," p. 67.

the latter gas in both the liquids was tried. Thirty cc. of pure ethylene were found to be practically all absorbed in the acetone, so for this purpose this reagent was useless. Similarly when 100 cc. of ethylene were treated with an excess of 95 per cent. ethyl alcohol a residue of less than 10 cc. was left, so this method was also inefficient.

Since Nordhausen acid is such a good solvent for ethylene,¹ it seemed possible that it might first remove the ethylene and leave the acetylene. To try this 56 cc. of known pure acetylene were passed several times into Hempel pipette which was filled with Nordhausen acid and after two passages, over 60 per cent. of the acetylene was absorbed, showing that this reagent also failed in the required work.

Although ethylene is soluble in ammoniacal cuprous chloride, it produces no precipitate, while, as is well-known, and has been previously shown, acetylene does form an insoluble compound. Hempel recommends the following method for estimating the amount of acetylene in a mixture:² 'pass the gas through ammoniacal cuprous chloride, collect the red precipitate of $(\text{Cu}_2\text{C}_2\text{H})_2\text{O}$, redissolve it after washing, and determine the copper by gravimetric methods.'

This recommended itself as a method of separating acetylene and ethylene, since the latter gas would form a soluble compound which would pass through into the filtrate. Of course the amount of acetylene corresponding to the weight of copper obtained was easily determined.

This method was tried and retried with good success, the only source of error being the possibility of loss through too rapid passage of the gas, and the only objection being the amount of time consumed. This objection was so serious that the method was abandoned for the quicker one described later.

The process was carried out as follows: the two gases were collected, thoroughly mixed in the Elliott apparatus and then passed to the graduated burette of an ordinary Hempel pair. A train of 6 5-inch U-tubes was set up and attached to the burette. This form of absorption tube is desirable on account of the ease with which the precipitate may be removed from

¹ Hempel, "Gas Analysis," p. 180.

² Hempel, "Gas Analysis," p. 183.

it. It was found desirable to use a tube having a bulb blown on each limb about one-third of the way up from the "expanded" bend. This tended to prevent particles of the precipitate from being carried up mechanically into the connecting tubes.

The leveling burette of the pair then served to force the gas through this train. When all the gas had left the burette a current of hydrogen (washed in silver nitrate solution and then in sulphuric acid) was passed through the train serving to cause complete contact of gas with solvent. After the first, nitrogen was substituted for the hydrogen, but either worked equally well.

The precipitate copper acetylide was removed, washed till no test for copper was obtained with the filtrate, after which the precipitate was dissolved in chemically pure hydrochloric acid, evaporated with a few cubic centimeters of concentrated sulphuric acid till sulphur trioxide fumes were evolved. Then it was diluted to proper bulk and the copper determined electrolytically.

Analyses thus made corresponded as closely as could be desired with the amount of copper corresponding to the known volume of acetylene which had been taken.

As before said, it seemed desirable to find a quicker method for the separation of ethylene and acetylene, and the effect of another good solvent of acetylene was tried on ethylene.

The solution used was ammoniacal silver chloride. This was made by dissolving 10 grams of silver nitrate in half a liter of water, making the solution barely acid with hydrochloric acid and then slightly ammoniacal. The clear solution thus obtained proved to be an excellent solvent of acetylene although it is slower in its action than ammoniacal cuprous chloride. Consequently greater care must be exercised to make sure that all acetylene is removed.

The compound formed by the solvent action is according to Lewes, Ag_2C_2^1 and not $\text{C}_2\text{H}_2.\text{Ag}_2\text{O}$ as stated by other authorities.

Having thus seen that this reagent was such a satisfactory

¹ Lewes, "Acetylene," p. 154.

solvent for acetylene it remained to try its action upon ethylene. When 26 cc. of known ethylene were treated with an excess of ammoniacal silver chloride, repeated trials showed that only two-tenths of 1 cc. were absorbed.

So although there is not absolute insolubility of the ethylene the method was admirable for its quickness and, of course, infinitely more accurate than using ammoniacal cuprous chloride.

Ammoniacal silver nitrate was also tried. This solution was made up of 5 grams of silver nitrate in 300 cc. of water and then ammonia was added to alkaline reaction. Practically the same result was obtained as when the chloride solution was used.

Now although it had been proved that, when taken separately, one gas is soluble and the other not, it was deemed best to try a mixture and see if it then worked equally well.

Hence a mixture of 29.2 cc. of ethylene and 37.3 cc. of acetylene were taken and treated with the silver solution. The residue left corresponded closely with the volume of ethylene taken, thus showing conclusively that a mixture of ethylene and acetylene may be readily separated by this method. Fractional per cents. of ethylene might be lost and for such small amounts, there seems nothing better than recourse to the gravimetric determination of the copper corresponding to the acetylene present, but this is not necessary for ordinary work.

It also seemed desirable to see if a mixture of ethylene and acetylene could be separated, when they react with bromine, by means of the difference between the substances formed.

Ethylene produces with bromine, ethylene dibromide, $C_2H_4Br_2$, while acetylene forms acetylene tetrabromide¹ (or tetrabromomethane), the formula of which is $CHBr_2$.

These two compounds having been formed, the wide difference in both boiling- and freezing-points suggested a means of separation. Ethylene dibromide freezes at $0^\circ C$. while the tetrabromomethane does not solidify above $-20^\circ C$.

On mixing these two substances, however, no solidification

¹ Reboul : *Annalen* **124**, 269.

took place even at so low a temperature as -12°C. , so this method of separation could not be used.

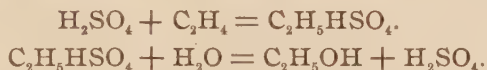
As there is a wide range between boiling-points, separation by fractional distillation was simple. $\text{C}_2\text{H}_4\text{Br}_2$ boiling at 25.5°C. at 9.38 mm. pressure, and CHBr_3 at 137°C. at 36 mm. pressure.

Another investigation was undertaken to see if by passing a mixture of acetylene and ethylene through strong sulphuric acid it were possible to produce alcohol.

Even when ethylene is pure, F. Wood¹ throws much doubt upon the possibility of producing ethyl alcohol by this method and it seemed desirable to see what result would be obtained when the ethylene was mixed with acetylene.

The latter gas to some extent is supposed to pass through unabsorbed, and this was found to be true; the issuing gas was deodorized but was still acetylene. That which absorbs should, on dilution and distillation, yield croton aldehyde ($\text{C}_4\text{H}_6\text{O}$) with a boiling-point of 104° to 105°C.

Ethylene, by the following reactions, should yield alcohol by the same treatment. (Consult Berthelot.)²



When hot sulphuric acid (165°) was used as an absorbent considerable sulphur dioxide was formed and the liquid turned black.

After absorbing the mixed gases for several hours, the acid was diluted and distilled with steam and the first fraction, which was evidently simply water, came over at 100°C. The temperature, moreover, rose no more and consequently no higher boiling-point liquid was obtained showing the absence of croton aldehyde.

Mr. Wood's objections seem, therefore, to be substantiated, and evidently it is not so easy as is usually supposed to transform ethylene to alcohol, especially if the gas be mixed with acetylene. Cold Nordhausen yielded no better results.

Run XIV was the first of a series in which was produced a

¹ Chem. News, 1898, p. 308.

² Compt. Rend., 50, 806 and 54, 515.

mixed aluminium calcium carbide which it was hoped might yield a gas other than methane or acetylene.

The charge used was not that given by Moissan,¹ but one composed of 112 grams of calcium oxide and 72 grams of coke which was found to be more satisfactory.

By calculation this mixture ought to produce 129 grams of calcium carbide. The molecules of this are to those of aluminium carbide as are 144 to 64. Therefore, in order to produce the proper amount of aluminium carbide, 49 grams of metallic aluminium (turnings) and 17 grams of coke were used.

This was heated for five minutes at 150 amperes and 70 volts. The product was not homogeneous. It consisted of yellow glancing plates of aluminium carbide coated with the black calcium carbide. An analysis of the gas evolved from this substance placed in dilute hydrochloric acid showed nothing but acetylene and methane.

In Run XV, in order to obtain a more homogeneous mixture, oxide of aluminium was used instead of the metal. The compound used was an artificially prepared oxide containing a slight amount of moisture and some silica, but otherwise very pure.

The charge was made up of enough of the oxide to be equivalent to the amount of metal which had been used in Run XIV, that is, it consisted of 100 grams of Al_2O_3 and 53 grams of coke; so the complete charge was made up of 112 grams of lime, 100 grams of alumina and 125 grams of coke.

This was heated for ten minutes at 150 amperes and 70 volts. The product was iridescent on fracture and although much more homogeneous than that obtained in Run XIV there were many parts composed wholly of yellow aluminium carbide. Neglecting these latter and using only the homogeneous parts, a gas analysis from dilute hydrochloric acid was made. One hundred cc. of this gas were all absorbed in ammoniacal silver chloride showing that it was all acetylene. Therefore, it seemed that what aluminium carbide had formed had stayed unmixed and the rest of the mass was simply calcium carbide. However an interesting fact was here noted,

¹ "Le Four Electrique," p. 290.

near the aluminium carbide masses, buttons of metallic aluminium were found. This metal, in this and in subsequent runs, often sprouted from the still warm mass and formed globules on the outside surface.

These globules showed their metallic nature by being unacted upon by water, were easily soluble in dilute warm hydrochloric acid, were quite malleable and showed crystalline character under the microscope. On qualitative analysis they proved to be elementary aluminium slightly contaminated with iron. Quantitative analysis showed the composition to be 99 per cent. metal and the rest iron and mechanically enclosed carbon.

Since it was found that this metallic aluminium was produced it seemed necessary to know whether ethylene would be produced by the action of dilute hydrochloric acid upon a mechanical mixture of calcium carbide and metallic aluminium. This was tried and 98 cc. of such gas left 5.5 cc. out of ammoniacal silver chloride and the same volume remained after treatment with bromine. So the residue after the acetylene was removed contained no ethylene and was simply hydrogen.

Run XVI differed from the previous one only in doubling the charge and increasing the time. This quantity so completely filled the furnace that the electrodes were covered and the charge being a fair conductor no arc formed, and the action was thus changed to one resembling a resistance type furnace. It was found that this required a longer heat, that is, a change from ten to twenty minutes, but this seemed beneficial as the charge was heated throughout and a larger yield of the metal resulted.

Analyses of the carbide mass were made both with silver solution and gravimetric determination of the copper precipitated by the acetylene which proved the product to be nothing but calcium carbide mixed with nodules of aluminium carbide. It presented a different appearance from ordinary calcium carbide being of silver-gray color and much softer than usual. With dilute hydrochloric acid or water, nevertheless, it would yield nothing but acetylene.

Considerable of this gray mass was decomposed by water and the calcium hydrate dissolved away with dilute acetic acid. This was done to see if metallic aluminium was disseminated throughout in the form of fine grains. It was not, however, all that was ever formed was always collected in some central mass near the aluminium carbide. Neither of these ever mixed with the calcium carbide.

The brass yellow nodules apparently aluminium carbide, proved, on analysis, to be very nearly a pure sample. Twenty-one cc. of gas from one nodule, which was treated with dilute hydrochloric acid, left $18\frac{1}{2}$ cc. from the acetylene absorption and none of this was soluble in bromine, and later was proved by explosion to be methane.

Although the gas analysis had shown no signs of ethylene in the gas evolved from the product of Run XVI, several other tests for it were thought to be advisable.

The first tried was the absorption of a large amount of the gas in bromine. The generation was accomplished in an Erlenmeyer flask kept cool by being immersed in water. The evolved gas was then washed in water, dried over phosphorus pentoxide, passed into an ordinary Drexel wash-bottle and any bromine fumes issuing from this were absorbed in caustic potash solution.

About 200 grams of the carbide were thus decomposed, and about 2 ounces of liquid bromine used as an absorbent. This latter was nearly decolorized and the remainder was neutralized with sodium carbonate. The resulting oil was washed with water and dried with calcium chloride.

As it had already been shown that a mixture of ethylene dibromide and tetrabromethane could not be separated by freezing, fractionation was resorted to. Diminished pressure (about 36 mm.) was used, but there was no evidence of any distillate corresponding to ethylene dibromide.

The specific gravity of the oil was taken before fractionation and although it was a little below that of tetrabromethane (which is 2.97) there was not enough difference to warrant saying that there was a mixture.

The specific gravity of the gas by the diffusion method of

Bunsen¹ and also by direct weighing were tried, but no results tending to show the admixture of any other gas were obtained.

In the light of these results, further attempts to produce ethylene by this means were abandoned and attention turned towards producing conditions which should better the yield of aluminium.

It has already been suggested by some authors that "bodies exothermic on decomposition if they are mixed with the charge tend to help reduce oxides of the metals." Acetylene and calcium carbide are examples of such bodies.

Knowing the foregoing, it is doubtless true that the aluminium produced in the previous runs was reduced as follows :



or by



The (at least theoretical) impossibility of reducing oxide of aluminium by simple carbon is wholly on thermochemical grounds, and therefore anything evolving heat on decomposition must tend to help the reduction.

Richard says :² "It is well known that alumina may be in contact with carbon at a white heat and yet not be reduced by it," and gives data³ showing the large amount of heat given out by the decomposition of acetylene. Therefore, there seemed no doubt that this metal was produced by the second of the preceding reactions.

Dr. Hunt, on the contrary, holds that alumina will be reduced by charcoal alone and that some of the metal will result even in the absence of some substance like copper to alloy with it. This idea however, although shared by Chappelle,⁴ does not seem to be held by many authorities.

A notable example of one holding the opposite opinion is Dr. Hempel⁵ who states that reduction of alumina by carbon alone is highly improbable on thermochemical grounds.

¹ Wiedermann-Ebert, "Physikalisch Praktikum," p. 102.

² Richards, "Aluminium," p. 242.

³ Richards, "Aluminium," p. 241.

⁴ Chem. Ztg., 1888, 12, 391.

⁵ Compt. rend., 1854, 38, 358.

In Run XVII, the first change was made in which the charge and current were kept the same as in Run XVI, but the time was increased from twenty to forty minutes. This was very unfavorable and absolutely no aluminium could be found in the product.

In Run XVIII, the charge was made up of 112 grams of calcium oxide, 100 grams of aluminium oxide, and 125 grams of coke. This was heated for fifteen minutes at 150 amperes and 70 volts. The result was some metal but less than was formed in Run XV.

In Run XIX, it seemed desirable to decrease time, and also the amperage. Consequently a charge the same as in Run XVIII was given 100 amperes and 40 volts for five minutes. As no aluminium resulted the mass was reheated for five minutes more with the same current and still no metal was formed.

In Run XX, since in Run XIX it had been evident that more current was needed, the usual charge of 112 grams of lime, 100 alumina, and 125 grams of coke were subjected to a current of 275 amperes and 45 volts for five minutes. This produced no metal, but on reheating for three more minutes with the same current, a fair sized button of aluminium resulted.

In Run XXI, a resistance furnace was employed having electrodes 2 inches in diameter connected with a quarter inch carbon rod. About this a furnace was built up and filled with the charge which consisted of 448 grams of lime, 400 grams of alumina, and 250 grams of coke. The current used was 100 amperes, and 95 volts.

A good fusion resulted in five minutes, and after five minutes more the mass was quite liquid and ran out of the furnace through the cracks. This product differed from the previous ones in being all black instead of gray, in containing no aluminium, in being only slowly acted upon by water hot or cold or by cold dilute acids. Hot dilute acids, however, acted upon it with some vigor.

This product was extremely interesting in its action in air and will be referred to again at length after Run L.

The analysis of the gas obtained from this product and hot dilute hydrochloric acid, showed, after treatment with ammoniacal silver chloride solution, a residue of 16.4 cc. from the original sample of 100 cc. This residue was not absorbed at all by bromine which showed it to be methane or possibly hydrogen from the action of the acid upon some metallic aluminium.

Run XXII, was an exact repetition of Run XVI as more of that product was needed for investigation.

Instead of producing the calcium carbide in the product a trial was made in Run XXXII of the effects of acetylene introduced through a cored electrode while the furnace was in action. A charge of 150 grams of alumina and 60 grams of coke (a little over the theoretical amount) was used and this was given 150 amperes and 60 volts for twelve minutes.

The product was not well fused looking more like cindered coke than a good fusion. It was covered with a white fibrous material probably sublimed alumina or silica from the alumina. There was an absolute lack of metal in all parts of the charge and, although some deposited carbon gave evidence of decomposed acetylene, there evidently had not been enough heat from such decomposition to effect any reduction.

This is an interesting result for if alumina cannot be reduced with the aid of decomposing acetylene it hardly seems possible that statements affirming its reduction by carbon alone can be true.

In Run XXXIII, the effect of adding calcium carbide, previously produced, was tried. The charge was composed of 150 grams of alumina, 60 grams of coke, and 100 grams of calcium carbide. This was given 175 amperes, and 70 volts for five minutes. This produced incomplete fusion so it was reheated for five minutes more, when a small yield of metal was obtained, but it was so small that the whole mass was returned to the furnace and heated for five minutes more. At the end of this time there was considerable aluminium carbide and a much larger yield of the metal; which, as in previous work, was found associated with the aluminium carbide.

To substantiate previous results obtained when the carbide had been made in the charge, all this product was returned to the furnace and reheated for six minutes more. This time there was no metal to be seen, which again proved that long heating is not favorable to the production of the metal, in fact it is fatal.

A gas analysis from this final product showed 1.8 cc. residue after treating 100 cc. with ammoniacal silver chloride. This residue was insoluble in bromine.

In Run XXXIV (which should be compared with Run XV) a change was made in the composition of the charge and a large proportion of coke was used. That is, the charge was composed of 100 grams of alumina, 112 grams of lime, and 200 grams of coke. This was heated for five minutes with 150 amperes and 60 volts, and then reheated for five minutes more at 200 amperes and 65 volts. The results here were entirely negative; there was no fusion and naturally no metal whatever resulted.

In Run XXXV, a change was made in the proportion of alumina, the charge being made up of 112 grams of lime, 175 grams of alumina, and 125 grams of coke. This was heated at 250 amperes and 80 volts for eight minutes. This gave a good fusion and a product which evolved gas freely, but it did not materially increase the yield of aluminium over what had been previously obtained.

One hundred cc. of gas from this product left 6.7 cc. residue out of ammoniacal silver chloride and this residue was insoluble in bromine.

In Run XXXVI, an increase was made in the proportion of lime, the charge being composed of 200 grams of lime, 100 grams of alumina and 125 grams of coke. This was heated for nine minutes at 200 amperes and 60 volts. The product was practically all calcium carbide.

In Run XXXVII, a return was made to the idea of introducing previously formed carbide into the charge. This time the amount of carbide was doubled, and the charge was made up of 150 grams of alumina, 60 grams of coke and 200 grams of calcium carbide. This mixture was heated for nine min-

utes at 200 amperes and 50 volts. This gave the best yield of metal thus obtained and as usual it was found associated with the carbide of aluminium.

In Run XXXVIII, it was shown rather conclusively that this associated yellow substance was formed from the metal, not the metal from it. To accomplish this, the product from Run XXXVII was freed from all metallic globules, an equal weight of calcium carbide added and the whole reheated at 200 amperes and 45 volts for twelve minutes. There was no more metal produced showing that the yellow crystals are not thus reduced.

In Run XXXIX, the effect was tried of decreasing the time which had been used in Run XXXVII. The charge remained the same, the amperage was increased to 275, the voltage to 50, and the length of run cut down to five minutes. This was evidently a change in the right direction for the best yield of metal yet obtained was the result. It was associated as usual with the nodules of aluminium carbide.

In Run XL, a distinct change was made and the coke was omitted from the charge, the reduction being accomplished simply by the decomposition of the calcium carbide. The charge of 150 grams of alumina, and 200 grams of calcium carbide was intimately mixed and heated similarly to that in Run XXXIX; that is, for five minutes at 275 amperes and 80 volts.

This gave fully as good but no better yield of metal than that obtained in Run XXXIX. One peculiar effect obtained was the lack of the yellow aluminium carbide.

During the run much gas, burning with an intensely bright flame, was evolved from the furnace. This evolution had nearly ceased when the current was turned off.

In Run XLI, a trial was made of the effect of an increased amount of calcium carbide; at the same time the current was cut down to 250 amperes and 70 volts, while the length of the run remained the same. The charge was made up 150 grams of alumina, and 400 grams of calcium carbide. The result was about the same as in Run XL, where there had evidently been enough carbide and the increase was of no benefit.

In Run XLII, since increase of time did not affect the yield of metal, an increase of time was tried. Run XL was duplicated except that the time was changed from five to seven minutes. This was distinctly a poorer method for almost no metal was produced. There was, however, considerable aluminium carbide formed which, of course, substantiates previous results by showing that the carbide forms from the metal and not the reverse.

In Run XLIII, the experiment of using less carbide was tried by heating a charge of 300 grams of alumina, and 200 grams of calcium carbide for five minutes at 225 amperes and 70 volts. This proved ill-advised as the amount of metal produced was much smaller than usual.

In Run XLIV, as a matter of interest, the effect of adding coke in larger quantity than had been used in Run XXXIX was tried. The alumina and carbide were kept in the same amounts, but 120 grams of coke were used. This mixture was heated for five minutes with 250 amperes and 60 volts, and then reheated for five minutes more. It proved impossible to produce fusion and no metal resulted.

In Run XLV, the same proportions of alumina and carbide were maintained as in Runs XXXIX and XLIV, but the coke was cut down to 30 grams. The run was for five minutes with the same current as in the previous trial. This gave a good yield of metal but was no improvement on that obtained in Run XXXIX or in Run XL.

Run XLVI was identical with XLV except that the current was maintained for ten minutes. This was an improvement and the increase in the amount of metal produced was marked. There was much of the aluminium carbide, however.

In Run XLVII, the modification next attempted was to increase the amperage decidedly. The charge was kept the same, that is, 150 grams of alumina and 200 grams of carbide with 30 grams of coke. The amperage registered 325 with a voltage of 70. This was maintained for twelve minutes and a perfect fusion and the largest yield of metal yet obtained was the result.

The evidence gathered thus seems to point to the necessity of high heat and, in the hope that there might be a saving in energy, and thus make more heat available from the same amperage, 2-inch electrodes were substituted for the 1-inch ones previously used.

In Runs XLVIII and XLIX, the charges were kept as before and the amperage maintained 325 with a voltage of 80. Run XLVIII was for fifteen minutes and Run XLIX was for eight minutes. There was no appreciable difference in the yield of metal, however, so whatever saving in energy there might have been was not enough to affect the product.

There was yet one other point to be investigated before any final conclusion could be reached, and that was to settle conclusively whether the metal resulted from the carbide, or the latter from the former.

In Run L, to accomplish this, aluminium carbide was made as follows: 130 grams of metallic aluminium, and 45 grams of carbon were heated with 150 amperes and 60 volts for five minutes. Then 45 grams more coke were added and the current raised to 200 amperes and 65 volts, and maintained for ten minutes. A good yield of bright yellow crystals was obtained. This was then powdered and mixed with calcium carbide and coke. All were then finely powdered and intimately mixed.

The charge consisted of 10 grams of aluminium carbide, 10 grams of calcium carbide and 5 grams of coke; the current at the start was 200 amperes and 65 volts and was soon raised to 275 amperes and 70 volts, the whole heat lasted seven minutes.

As was expected from what had been previously observed, absolutely no metal was produced showing very conclusively that the metal is primarily formed and then it is not reduced from the carbide.

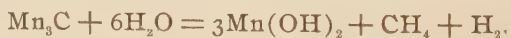
The conclusions to be drawn then from this series of experiments are as follows: (1) Aluminium oxide is not reduced by carbon to any appreciable extent even when both are heated to the extremely high temperature of the electric arc. (2) The addition of lime and the necessary excess of carbon

forms an alkaline earth carbide which in turn is decomposed. It being a body exothermic on decomposition it yields up a larger number of calories of heat and thus raises the temperature to such a degree that reduction of the oxide takes place to an appreciable amount. (3) The carbide may be made in separate reaction and added to the alumina, with or without carbon, but the presence of some carbon seems to increase the yield of metal. The production of the carbide in a separate reaction would, however, be condemned on economic grounds. (4) As regards time, anything over twelve or fifteen minutes is prejudicial to good results and converts the reduced metal to carbide in amounts increasing directly as the excess over the maximum admissible time increases.

The whole subject may be summed up as follows: results obtained favor the use of high amperage and voltage for not more than fifteen minutes. The presence of both carbon and a carbide of an alkaline earth is required. Air should be excluded. Lastly the amount of alumina should be considerably in excess of the theoretical amount of coke.

Beginning in Run XXXI an investigation was also made of the nature of the gas evolved from a mixed carbide of manganese and calcium.

When placed in water, manganese carbide is known to evolve no acetylene, but a mixture of hydrogen and methane.¹ This occurs by the following reaction:



Here also, if this was combined with calcium carbide, there seemed a possibility of interaction between the simultaneously evolved acetylene and the hydrogen or the methane. It was also probable that the mixed compound might directly evolve some gas like ethylene.

In Run XXXI, the charge for the manganese carbide consisted of 100 grams of manganese dioxide and 32 grams of carbon. That for the calcium carbide consisted of 112 grams of lime and 72 grams of coke. This mixture was subjected for twelve minutes to 150 amperes and 70 volts. The result-

¹ Moissan, "Le Four Électrique," p. 328.

ing product differed but little from ordinary calcium carbide in appearance except that it contained a bronze-like button in the center. This button evolved no gas in water, but was acted upon by cold dilute acids with evolution of hydrogen showing its metallic nature.

A sample of 100 cc. of gas obtained from the major part of the product was entirely absorbed by ammoniacal silver chloride showing it to be all acetylene.

It seemed evident from this run, since nothing but acetylene had been produced, that absolutely no manganese carbide had been present in the product. Consultation of authorities and runs made personally showed that manganese carbide needed quite different conditions for its formation compared with those needed for the calcium compound.

In Run XXXI, the manganese carbide had probably been decomposed before the calcium carbide was entirely formed.

To see if it were possible to avoid this decomposition Run LI was continued for five minutes only; otherwise the conditions were just the same. The product, however, was very similar to that obtained before. It contained the same metallic button and the rest of the product evolved gas from water, which by absorption in the silver solution, and also by the method of copper deposition, proved to be all acetylene.

A qualitative test of the metallic button showed it to be composed of elementary manganese contaminated with iron. As ordinary pyrolusite had been used, the presence of the iron can be understood.

It therefore seemed probable that a mixed carbide of manganese and calcium could not well be prepared, owing to the different conditions under which they should be formed. It also seemed probable that the calcium carbide exercised a reducing action and tended to produce metallic manganese just as metallic aluminium had been formed in previous work.

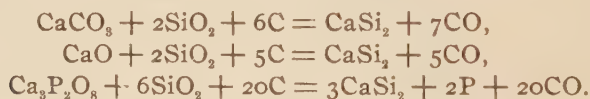
The foregoing ended the attempt to produce ethylene or similar compounds through the interaction of gases simultaneously evolved from mixed carbides and attention was turned to mixed silicides and carbides.

The silicides, principally known through one representative silicide of carbon (carborundum), are an interesting class of bodies analogous to the carbides and having the general formula of RSi_2 . In this, R represents any bivalent element. To quote M. Moissan, "Ces composés étaient mal déterminés et peu connus jusqu'ici."

These silicides may be made: (1) By the direct combination of the element used and elementary silicon; (2) by the method given in text-books, which is by fusing a metallic chloride with sodium chloride, sodium silicofluoride and metallic sodium; (3) by heating oxides, carbonates, phosphates, etc. with silicon oxide and carbon.

Moissan¹ uses the first method largely and has produced silicides of iron, chromium, etc., which are bodies not interesting for this work.

Jacobs,² however, has produced alkaline earth silicides according to reactions similar to the following, which seem to offer properties making them suitable to accomplish the end in view by combining them with carbides.



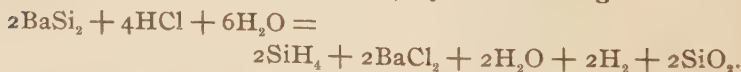
These compounds are found to decompose with water producing, not acetylene, but hydrogen according to the following:



Strangely enough dilute acids with calcium silicide do not produce gas according to the above, but form silicoacetylene by the following reaction:



The corresponding barium salt reacts differently producing silicomethane (or silicon hydride) by the following:

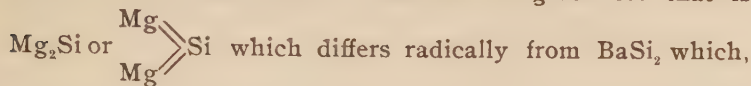


It is to be noticed that silicides made this way differ in for-

¹ "Le Four Electrique."

² U. S. Patent No. 656,353, August 21, 1900.

mation from magnesium silicide, as commonly known and spoken of in text-books. The formula given for that is



when written $\text{Ba} \begin{array}{c} \text{Si} \\ \diagup \quad \diagdown \\ \text{Si} \end{array}$, shows the relationship which exists be-

tween these bodies and the carbides, as for example, $\text{Ba} \begin{array}{c} \text{C} \\ \diagup \quad \diagdown \\ \text{C} \end{array}$.

The barium compound seemed the most likely to fulfill the desired conditions and that was first selected.

The witherite which had been used for making carbide in previous work was selected and should act as follows :



and with water it should react according to,



It was thought that this hydrogen in the nascent state would be very likely to combine with the acetylene changing C_2H_2 to C_2H_4 or to similar compounds.

In Run LVII, the first trial was made with a charge of 100 grams of witherite, 60 grams of silica and 43 grams of coke. This corresponded with the theoretical calculated amounts from the reaction for the silicide. For the carbide the usual charge as determined in Run VIII, was used; that is, 150 grams of witherite and 25 grams of coke. These two mixtures were intimately mixed and for seven minutes subjected to the heat of 150 amperes and 60 volts.

The product was blackish with a white crust on the surface. It was a slow gas producer in cold water, but quite vigorous action began when the lump was placed in warm water. Fifty cc. of this gas from warm water were treated with ammoniacal cuprous chloride. This, as shown by previous work, would absorb both acetylene and ethylene, and would simply show how much hydrogen there was present. The residue left was 32 cc. The absorption with the ammoniacal silver chloride was next tried; this would remove the acetylene

alone, and the residue here was found to be 39.5 cc. showing a difference of 7.5 cc. which must have been ethylene.

To prove it the remainder was treated with bromine and the absorption corresponded with the difference before noted ; that is, this 50 cc. of gas contained 7.5 cc. of ethylene or about 15 per cent.

This analysis was repeated several times with lumps from various portions of the fusion, and quantities of ethylene varying from 8 per cent. up to 15 per cent. were obtained, showing that the mass was not homogeneous and indicating an average of a little over 11 per cent. of ethylene.

As there was considerable excess of hydrogen in the gas here evolved it was thought possible that for this amount of silicide more carbide was needed which would give more acetylene to be acted upon.

Consequently in Run LVIII, the silicide charge remained unchanged and the carbide charge was increased to 225 grams of witherite and 37 grams of carbon. The amperage and voltage were kept the same but the time was increased to nine minutes.

The product was very much the same in appearance and evolved gas in a similar manner. On analysis, the gas evolved from hot water showed only about 2 per cent. of ethylene proving that such a charge was not desirable.

Another analysis of the product of Run LVIII was made by evolving the gas from dilute hydrochloric acid. As has been shown on a preceding page, such a reaction produces a mixture of hydrogen and silicon hydride, and it seemed interesting to determine whether this would change the yield of ethylene. It did not, as about 2 per cent. was found.

In Run LIX, since an increase of carbide had not proved advantageous, the carbide content was diminished. The silicide charge remained constant but the carbide charge was made up of 75 grams of witherite and 12 grams of coke. These two mixtures were then subjected for ten minutes to 150 amperes and 60 volts.

The product had the outward appearance of that obtained

in Runs LVII and LVIII, but it evolved less ethylene, only a fractional per cent. in fact.

In Run LX, the influence of the substitution of strontium for barium was tried. The reaction for the formation of the silicide is similar to that for barium ; that is,



By calculation from this the silicide charge was made up of 100 grams of strontianite, 81 grams of ground quartz, and 57 grams of coke. This was combined with a carbide charge of 150 grams of strontianite, and 50 grams of coke.¹ When this was well mixed it was subjected to 150 amperes and 70 volts for ten minutes.

The product, which was well fused, was a better evolver of gas than the barium compound. One hundred cc. of the gas, obtained by the action of hot water, showed 3.5 per cent. of ethylene, so nothing was gained by the substitution.

In Run LXI, one other trial was made in which the silica was doubled. Here the charge for the silicide was made up of 100 grams of strontianite, 162 grams of quartz, and 57 grams of coke, while the carbide mixture was 150 grams of strontianite and 50 grams of coke. This was heated for ten minutes with 150 amperes and 60 volts. As would have been expected from the presence of the extra silica, the product was much more pasty and viscous. It was a very poor gas evolver and what gas was produced was practically all acetylene.

In Run LXII, strontium having proved to be so poor a substitute, a return to barium was made. Here the effect of greater heat was tried, the charge being just the same for both silicide and carbide as in Run LXII. The mixture was subjected to 225 amperes and 70 volts for nine minutes. The product was similar to that produced before, and evolved gas very rapidly.

Several samples of this product taken from different parts of the cake were treated with hot water, and each time 100 cc. of the gas evolved was examined. The amounts of ethylene varied from 3 to 10 per cent. The foregoing figures

¹ Miossan, "Le Four Électrique," p. 301.

thus show that the extra heat used in this run is not necessary.

The residue left from bromine, in one of these analyses, was mixed with oxygen, and exploded as usual. There was an entire absence of carbon dioxide which proved that no marsh gas had been present and further calculation showed the hydrogen to have been 100 per cent. of the original volume exploded.

It was thought possible that the presence of an oxidizing substance in the water in which the mixture was placed might modify the gas evolved. Trials were made from solutions of chromic acid and hydrogen peroxide, but the results observed were precisely similar to those obtained with water alone.

The third and last possible combination was that of silicide and carbide of calcium.

The silicide is produced by,



Calculating from this, the charge should be made up of 56 grams of lime, 214 grams of quartz and 108 grams of coke. This was mixed with the usual carbide charge of 112 grams of lime and 72 grams of coke. The whole was then subjected to 200 amperes and 60 volts for eight minutes.

The product was not a good evolver of gas and what gas was produced was shown upon analysis to be all acetylene with the exception of 2 per cent. of ethylene.

This product was also tried with acid,—hot dilute hydrochloric being used. The gas thus evolved showed no ethylene whatever upon analysis; this might be expected when it is remembered that acid acts upon calcium silicide to produce the *solid* “silico-acetylene.”

Attention is now to be turned to the product obtained in Run XXI. It will be recalled that this was a very complete fusion, obtained by heating the aluminium-calcium carbide mixture in a resistance type furnace. The product was very compact and streamed out of the furnace, forming long, thick bands, black on the surface and a lusterless gray of fracture. It contained no agglomerated aluminium nor any large masses of its carbide.

This run was made on January 8th, and a gas analysis made then showed 16.4 cc. residue from the ammoniacal silver chloride solution, out of 100 cc. of gas evolved from hot dilute hydrochloric acid. This residue was unabsorbed by bromine and at that time was called methane and hydrogen.

As this analysis showed the absence of ethylene in the evolved gas, the sample was neglected as of no interest and remained in a partly filled bottle until February 12th when, on examination, the fractures were observed to be materially changed in appearance. They had changed from a lusterless gray to glistening greenish yellow in color, much resembling pyrites.

On February 14th, an analysis was made of the gas obtained from the substance which had stood in the bottle since January 8th. This should be compared with the analysis recorded above. The gas was evolved from dilute hydrochloric acid, and 100 cc. of it left 26 cc. out of ammoniacal silver chloride. This volume remained unabsorbed by bromine.

In the previous analysis, it will be noticed that the silver solution left a residue of 16.4 cc. from 100 cc. of gas, and that in bromine this volume remained constant. Consequently, while standing in the bottle for a month, the product had evidently absorbed some gas, insoluble in silver chloride and bromine.

In the light of this interesting fact, it seemed desirable to continue the analysis of the gaseous residue from bromine. Therefore, the 26 cc. were mixed with oxygen and air in the usual way and transferred to the explosion burette of the Elliott apparatus. The above figures together with the result of the explosion and subsequent absorption showed the gas evolved to have had the following composition :

	Per cent.
C_2H_2	74
N	21
CH_4	2
H	3
	100

The acetylene naturally came from the calcium carbide, the methane from some aluminium carbide, the hydrogen from some grains of metallic aluminium and the nitrogen must have been absorbed from the air.

The next step was to allow the product to "weather" as completely as possible and consequently a generous amount of it was spread in a thin layer for several days.

From its properties, the new product seemed to be a combination of aluminium and nitrogen. The properties of Al_2N_3 , the nitride commonly known, are described as follows:¹ "Small golden crystals, softer than glass, turning sulphur-yellow in moist air and breaking up with evolution of ammonia. Heated in air it turns to the oxide. Acids and alkalies cause quick decomposition."

Again, Moissan says:² "Nitrogen, pure and dry, is without action upon calcium carbide even at 1200° C."

So, since it seemed probable that this was a compound of nitrogen and aluminium, it was very likely that as it stood in contact with the calcium oxide formed by the decomposition of the carbide of calcium, some ammonia would be evolved. Consequently, besides that which was exposed in trays, a sample of about one hundred grams of the powdered product was placed in an Erlenmeyer flask and air under pressure was first washed in water in a Drexel wash-bottle and then passed over the powder. From here the air passed into 10 cc. of normal (exact) HCl diluted to about 50 cc.

Air was thus passed continuously for five consecutive days, but the hydrochloric acid at the end of that time took exactly 10 cc. of normal (exact) caustic soda solution to neutralize it. This, of course, showed that no ammonia had been evolved.

After three days of exposure to the air in a porcelain tray, the sample there placed had completely disintegrated and turned to a yellow-green powder which, as before said, very closely resembled pyrites. This green powder, under the microscope, was markedly crystalline. It loses its color and becomes grayish, but evolves no ammonia when it is heated in a mat-

¹ Dammer, Vol. 3, p. 105.

² "Le Four Électrique," p. 295.

trass. It dissolves readily in hydrochloric acid, leaving a residue resembling graphite. Hot caustic potash does not dissolve it, nor, so far as the sense of smell can detect it, does it cause evolution of ammonia. However, when the metallic salts had been removed from the hydrochloric acid solution, Nessler solution showed the presence of ammonia in small amounts. Nessler solution also showed the presence of small amounts of ammonia in water in which the green powder had been boiled.

Some of the powder was placed in a tube and heated, and the resulting gas passed into water. On nesslerization this water also showed the presence of traces of ammonia.

After this, some of the powder was placed in a combustion tube, warmed, and steam passed over it and the issuing gases passed into dilute hydrochloric acid. This, too, gave negative results.

The next reagent tried was alkaline permanganate solution; this was added to considerable of the powder and the whole boiled for some time. Any resulting gases were passed into dilute hydrochloric acid in order to fix the ammonia. Qualitative tests with the solution showed no ammonia in appreciable quantities.

The powder was then subjected to the Kjeldahl process. About 25 grams of the weathered product were placed in a Kjeldahl flask and covered with concentrated sulphuric acid. Great heat was evolved and white fumes (but not sulphur trioxide) were given off. These soon stopped after which heat was applied for twenty minutes. Solid potassium permanganate was then added and, after cooling, water was added, and the whole transferred to a boiling flask. It was then made alkaline with potassium hydrate and boiled, the distillate being caught in dilute hydrochloric acid. Neither nesslerization nor boiling with caustic potash showed any appreciable amounts of ammonia.

The action of nascent hydrogen was next tried. The powder was mixed with water, and sodium amalgam was added. This caused no evolution of ammonia.

Since the possibility of the evolution of ammonia from this

substance was thus shown to be improbable, attention was turned to analyzing the gas evolved from it under various conditions.

The most interesting point was to determine the increase in nitrogen content after the original product had been exposed for several days to the air.

A sample was taken which had been exposed four days, the green powder was treated with hot dilute hydrochloric acid, gas was evolved rapidly and a sample of 31.4 cc. was taken which left 22.2 cc. residue from ammoniacal silver chloride solution. Bromine, as would be expected, caused no absorption in the residue which was then exploded and subsequently treated as usual. The results of the complete analysis are expressed as follows :

	Per cent.
C_2H_2	29.3
CH_4	31.2
H	0.482
N	38.6
	99.582

So the nitrogen had nearly doubled during these four days of exposure.

An analysis was next made of the gas evolved by treating the green powder with hot water. The sample taken had weathered five days. Thirty and two-tenths cc. of the gas were taken and treated with ammoniacal silver chloride solution, bromine, and then exploded as usual. The result of this work was as follows :

	Per cent.
C_2H_2	14.5
CH_4	38.7
H	8.2
N	38.4
	99.8

The decrease in acetylene should be noticed as the result of some extra exposure to the air. Also it is evident here that the nitrogen is evolved just the same as when acid is used,

that it reached its maximum content in three days and had absorbed no more by increased exposure.

The influence of heat on the powder was next investigated and as a preliminary test some of it was heated in a matrass and the gas evolved was collected in the Elliott apparatus. A sample of 17.7 cc. was thus collected and the acetylene absorbed as usual; there proved to be 3.9 cc. of this gas. In order to see if possibly any oxygen from the air left in the matrass was present, alkaline pyrogallate solution was next used. There was an absorption of only 0.7 cc. which showed the gas to be quite pure.

Since the powder might not have been dry, the water thus held might react as usual on the mixed carbides and it therefore seemed possible that the above gas might have been evolved not merely through the action of heat. Such a condition did not seem very probable, for aluminium carbide evolves gas very slowly, even with plenty of water. Moissan¹ found that in twelve hours only 7.5 cc. were evolved, whereas in the foregoing, 17.7 cc. were collected in a few minutes.

Nevertheless it seemed best to be sure and consequently for the complete analysis the sample of the powder was dried at 110° C. for six hours. Twenty cc. of gas from this dried powder were obtained and the acetylene removed as usual and the residue, insoluble in bromine, was exploded. As a result the following was obtained:

	Per cent.
C ₂ H ₂	15.0
CH ₄	22.8
H	32.8
N	29.3
	99.9

Finally, a good sample of the green powder was selected, and from it a quantitative analysis was made. The weighed sample was heated for eight hours at 110° C. and lost nothing in weight, thus showing absence of moisture. It was then dissolved in aqua regia and the insoluble black residue, which was 1.9 per cent. of the whole charge, filtered off. It re-

¹ "Le Four Électrique," p. 325.

sembled graphite and, in order to see whether it was that substance, it was transferred to a combustion boat and heated for several hours in a current of oxygen in a furnace. No change in weight resulted. Consequently it was fused with sodium carbonate, dissolved in acid, evaporated to dryness, dehydrated and the acid solution combined with the original aqua regia solution.

The result of the whole analysis was as follows :

	Per cent.
Moisture	0.00
Silica	1.04
Ca(OH) ₂	69.6
Aluminium compounds	29.3
	99.94

It was evident from the figures obtained that the aluminium was present as more than one compound, doubtless as a mixed hydrate and nitride. It is this complex nature of the powder which makes it hard to say anything definite regarding the formula of the nitrogen compound thus formed.

However, this much seems evident, first, that when the product of Run XXI was exposed to the air, it absorbed from it nitrogen in varying quantities according to the time of exposure and amount of air available; second, that since calcium carbide is not acted upon by nitrogen, even at 1200° C., that it was not a calcium nitride which formed; third, that owing to its similarity in properties to Al_2N_3 , it probably is a compound of nitrogen and aluminium; fourth, that since aluminium carbide alone is not decomposed by nitrogen¹ it must be the presence of the calcium carbide which enables the absorption to take place; fifth, that this compound when formed yields up the absorbed nitrogen by heat alone, by the action of hot water and by the action of hot dilute acids. It does not, however, yield ammonia either on exposure to the air, by the action of water, alkalies, acids, or oxidizing agents. It is therefore not Al_2N_3 .

The nitrogen left after one of the analyses was transferred to a spectrum tube and rarefied, and its spectrum obtained.

¹ Moissan, "Le Four Électrique," p. 324.

This was done with the intention of seeing if it contained any such gas as argon, but the results showed the presence of nitrogen only.

PART II.

The ability of certain metals, notably magnesium and titanium, to combine directly with nitrogen to form nitrides such as Mg_3N_2 and Ti_3N_4 is a known fact. As directed in text-books they may be prepared first, by producing the metallic element and then combining it with the nitrogen (as such, or as ammonia); or second, through the use of oxides of the element and ammonia; or third, through the use of such compounds as ammoniochloride of titanium. So such processes either involve the sometimes expensive process of first producing the metal, or they *employ* ammonia, not produce it from nitrogen.

It therefore seemed desirable to see if some of the nitrides known to decompose readily and yield ammonia could not be produced directly in the electric furnace.

The "fixation" of atmospheric nitrogen to form cyanides is now an accomplished fact,¹ but the commercial production of nitrides capable of breaking up into ammonia is as yet unsolved. Brennen says:² "The fixation of atmospheric nitrogen is an industrial problem to be compared with that involved in the manufacture of ammonia soda or water gas, each of which passed through quite as discouraging an experience before attaining success; as has, so far, been the lot of the nitrogen question."

Of course, no one need be told of the value of a process which would produce such a nitride, so, in the first three of the next set of runs, an investigation was made of the possibility of making the compound Ti_3N_4 in the electric furnace.

The three possible nitrides of titanium, according to Friedel and Guerin, are Ti_3N_2 , Ti_3N_4 , and Ti_2N_2 .

The material used for the preparation was powdered rutile and coke. In Run XXVIII, 100 grams of the rutile were mixed with 50 grams of coke, and heated for fifteen minutes

¹ Jacobs, U. S. Patent, 657,937.

² J. Am. Chem. Soc., Vol. 2, 1889.

at 175 amperes and 70 volts. Air was introduced from the start, being led in through the annular opening in one of the electrodes.

This gave a reddish black product, which, when boiled with water or caustic potash, gave negative results. Dilute hydrochloric acid gave a slow evolution of gas smelling like impure hydrogen and it doubtless was that.

In Run XXIX, since the heat had evidently not been sufficient in the previous run, the charge was kept the same, but the amperage was increased to 200 and the voltage to 70. This was continued for ten minutes, producing some fused lumps which, on the outside, had the appearance of limonite, but on fracture they showed fine reds and blues.

Some of this product was powdered, and 4.6 grams of it were placed in two boats and put in a combustion tube and heated in a gas furnace. Hydrogen gas, washed in water and silver nitrate and then dried in sulphuric acid, was passed over the heated boats. The issuing gas was passed into 100 cc. of N/1 hydrochloric acid contained in a Drexel wash-bottle. After several hours, the acid was titrated with normal caustic soda, and was found to be unaltered in strength, thus showing that no ammonia had been formed, and consequently that no Ti_3N_4 had been present.

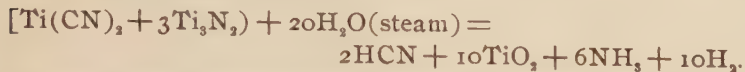
Some of the original product was fused with caustic potash, yielding very faint traces of ammonia, but treatment with boiling water, hot caustic potash solution, hot dilute sulphuric and hydrochloric acids yielded negative results.

It is interesting to note, however, that the acid solutions, upon standing over night, presented a greenish yellow appearance by reflected light and a violet color by transmitted light. This is one of the properties of a suspension of Ti_2N_2 in a state of fine division, and since no Ti_3N_4 formed, it is probable that the former is the only nitride which will form in this way.

Some of the original product was also suspended in water to which sodium amalgam had been added. This was heated, but no ammonia was detected either by odor or the use of turmeric paper.

A test for the presence of any cyano-nitride was also made

as follows: Some of the product was heated to a dull red in a combustion tube and steam passed over it. By this means, if any cyano-nitride is present, mixed ammonia and hydrocyanic acid should form by



No such result was obtained, however, proving the absence of the cyano-nitride.

It is therefore evident that such a process as this produces no cyano-nitride, and, since there is no ammonia produced from the product, as the color of the product is indigo-blue, as certain optical effects are produced on suspension of the substance in water, and as the titanium content is 77 per cent., it is probable that only one nitride is formed and that that is Ti_2N_3 .

In Run XXX, the effect of increased heat yet remained to be tried. Here the charge was the same as in the other two runs but the amperage was increased to 200, and the voltage to 70 and maintained for twenty minutes. In this run another change was made in the substitution of nitrogen for air. The nitrogen was prepared as usual by passing air over copper heated in a combustion furnace.

The gas was admitted throughout the run and after the current was shut off continued for five minutes. The furnace, filled with nitrogen, was tightly closed and allowed to cool down.

The product was one of great beauty and varied from indigo-blue flecked with bright red spots near the edges to brass-yellow at the point directly under the arc and in contact with the carbon bed of the furnace. This yellow part was extremely hard, and with no difficulty scratched corundum and carborundum. This part was doubtless the carbide of titanium TiC , or a mixture of it and the cyano-nitride, but the existence of the latter at the temperature reached in making this product is extremely doubtful.

According to Moissan, the determining factor as to the final product is the temperature. The blue oxide (not Ti_2O_3 , the formula is undetermined as yet) is formed at first, then

the nitride, then the carbide and lastly the metal results. He also states that at a temperature where titanium carbide or the metal is produced the existence of the nitride is no longer possible.

It therefore seems probable that in this run the product was a mixture consisting of the blue oxide, the copper-red nitride Ti_2N_2 , and the bronze-like carbide. It thus seems improbable that the desired nitride, that is, Ti_3N_4 , can be prepared directly from the oxide and nitrogen.

Calcium nitride corresponding to the formula Ca_3N_2 has been produced, but always through the production of the metal first, and subsequent absorption of the nitrogen.

No data being found regarding the possibility of producing the nitride directly from the oxide, it seemed desirable to make an investigation of the possibility of such a reaction.

Moissan¹ has been able to prepare the metal by simple reduction with carbon accompanied by distillation of the metal thus produced. Therefore as the reduction part is a simple process, far easier than the usual text-book methods such as electrolyzing the chloride, there seemed a probability that if nitrogen were supplied at the time of formation, two things would be accomplished by its introduction. First, the reduced metal would have less tendency to oxidize, as air would be largely excluded and this would tend to accomplish the same purpose as the distillation; second, the metal being thus preserved would tend to combine with nitrogen and give the nitride.

Its failure to do so seems explainable by one of two reasons: the reoxidation or volatilization of the metal; or, the wide range in temperature between the point which it is necessary to reach before calcium oxide is reduced by carbon and that necessary for the combination of calcium and nitrogen. The latter is very low compared to the former and the attempt to cause simultaneous reduction and nitrification, owing to the degree of heat which must be maintained to keep the reduction process in action, seemed to cause a complete transformation to carbide of whatever nitride is produced. The re-

¹ "Le Four Électrique," p. 292.

sults obtained which caused the above conclusions to be reached were as follows :

In Run L,II, the lime and coke were taken in the best proportion to produce metallic calcium which is 200 grams of lime to 43 grams of coke. This mixture was subjected to 200 amperes at 75 volts for seven minutes. The nitrogen used was "chemical" nitrogen prepared by heating sodium nitrite and ammonium chloride. It was collected in ordinary aspirator bottles and, before entering the furnace, was dried in calcium chloride towers.

The gas was not introduced until the charge had been heated for five minutes ; it was then continued to the end of the run, and for five minutes afterward.

The product was well fused and reddish on fracture. Some of it was boiled with water and the evolved gas was for some time passed into N/1 HCl. On boiling and titrating this solution the acid content was found to be unchanged.

From water this product evolved gas freely and 85 cc. of it were collected and treated with ammoniacal silver chloride. This volume was totally absorbed, showing the product to have been nothing but calcium carbide.

In Run L,III, the same charge was used as in L,II, but the amperage was reduced to 150 and the voltage to 60 and the time was for five minutes only. The nitrogen was introduced throughout the entire run. Except that in the air holes a silvery product was observed, the product resembled the previous ones.

However, 100 cc. of gas evolved from this when placed in water was collected for analysis but it was found to be totally absorbed by the silver solution. A quantity of the gas from boiling water was also passed into 10 cc. of N/1 HCl, but subsequent titration showed that no alkali had been evolved.

In Run L,IV, a modification was made in the furnace in the hope of remedying the first of the possible causes of failure, that is, the loss of the metal by volatilization. A carbon diaphragm was placed transversely in the box of the furnace and luted tightly to the sides and bottom. It contained a large hole for the electrode and four smaller holes placed around it.

The main part of the furnace was then luted air-tight and a cover without vent holes over the charge was affixed tightly. A charge of the same composition as formerly was introduced into the larger compartment and there the arc was made to form.

Of course, this would cause one chamber, in which was the charge, to be heated to a higher temperature than the other one. The desired end was for the metal to form under the arc, and then volatilize and pass through the holes in the diaphragm and into the smaller chamber which would be filled with nitrogen. The temperature there would presumably be hot enough to effect combination of the two and the nitride would result.

The heat was continued for five minutes at the same amperage as in the preceding run. On opening the furnace, nothing was found in the small chamber; and under the arc, nothing but the usual carbide was present.

As it is an accepted fact that an excess of lime is necessary in order to produce metallic calcium, this seemed to show that an excess of carbon had been present. As the carbon in the charge was not excessive in amount it seemed likely that the carbon of the furnace itself entered into the reaction.

In Run LV, consequently, a chalk furnace was used. The charge, of the same proportion as before, was subjected to 175 amperes and 60 volts for eight minutes.

The greater part of the product was simply carbide; but smaller masses, brownish in color, would, when boiled in water, yield sufficient ammonia to give a good test with Nessler's reagent. This, however, was the best result that could be obtained.

In Run LVI, a change was made and oxide of magnesium was used instead of lime. There was one well determined point in favor of using this metal, *viz.*, the difficulty with which it forms a carbide and the ease with which the carbide, after it has formed, breaks up at high temperatures.

Of course its readiness to volatilize and oxidize argued against it, as in the case of calcium, but it was hoped that the nitride might form before the metal escaped.

The charge was made up from the calculation of the theoretical amounts as follows: 85 grams of calcined oxide of magnesium, and 25 grams of coke. This was heated for ten minutes with 100 amperes and 60 volts. The product was not fused and no part of it with water or alkalies would yield ammonia.

Although such a process would have no economic value it seemed of interest to investigate the possibility of reducing nitrates to nitrides. If this were capable of being accomplished, nitrides not easily formed by absorption of nitrogen might be produced.

Magnesium nitrate was selected for trial, first because the properties of its nitride were known, and second, because its first action under heat is to change to a trimagnesium, nitrate, $\text{Mg}_3(\text{NO}_4)_2$. This substance is analogous to calcium orthophosphate which, as is subsequently shown, was so successfully reduced to a phosphide.

The magnesium nitrate was prepared by dissolving 400 grams of magnesite in 600 grams of nitric acid and crystallizing as usual. This salt melts in its own water of crystallization, so it was heated in a gas furnace till nitrogen peroxide fumes were evolved.

In Run LXV, 180 grams of this fused nitrate were mixed with 76 grams of coke which was the calculated amount of carbon by which to cause the reduction, according to



This mixture was heated for ten minutes at 200 amperes and 60 volts. As this produced no fusion, it was reheated for ten minutes at 235 amperes and 70 volts. This also produced no fusion and the product would evolve no ammonia from water or alkalies.

In Run LXVII, one more trial, using less current, was made. The charge was the same as in Run LXV. This was heated for five minutes (with no result) at 75 amperes and 55 volts. It was then reheated for five minutes at 100 amperes and 50 volts,—still no result. This was again heated at 150 amperes and 60 volts for five minutes and gave entirely negative results.

PART III.

Although phosphides do not possess great economic value, yet they are used to some extent and, consequently, any cheapening of the cost of their production is a matter of interest. In addition to this, their production through the direct reduction from phosphates is a matter little investigated and such data, therefore, is of value in itself.

Text-book directions, and for that matter actual production, depend upon the primary production of elementary phosphorus and the passing of its vapors over the oxide of the metallic element; or, again, through the direct union of a metal and phosphorus.

The phosphides best known are those of the alkaline earths and they are these very ones which may be made by direct reduction.

That indefatigable worker, Moissan, has recently produced a phosphide of calcium by a method similar to the one here recorded, but it was not discovered that he had done so until after this work, which was performed entirely independently, was finished.

There seems no reason why the phosphates should not be reduced to phosphides and it is a matter of some surprise, since the native phosphates are so abundant, that such a process has not been used before now.

The first attempt at such a reduction was made by using calcium orthophosphate in the form of bone-ash. One hundred and fifty grams of it were mixed with 45 grams of coke and the whole heated for ten minutes at 150 amperes and 50 volts. The result showed that this was insufficient heat and consequently the product was reheated for ten more minutes at 200 amperes and 60 volts. This product was well fused and evolved phosphoretted hydrogen freely when placed in water.

The use of calcium phosphate having proved so successful, the next investigation was that of the behavior of magnesium phosphate in producing Mg_3P_2 .

The most convenient phosphate of this metal was prepared by precipitating from magnesium chloride with sodium hydro-

gen phosphate in ammoniacal solution. This precipitate, when filtered and dried, was ignited to remove ammonia, yielding, of course, the pyrophosphate by the following reaction :



In Run LXVI, 200 grams of this pyrophosphate were mixed with 80 grams of coke, which was the calculated amount from the above reaction. This mixture was then heated for ten minutes with 225 amperes and 70 volts. The product would not evolve any gas when placed in water.

In Run LXVIII, consequently, less heat was employed. The same charge was employed and subjected to 100 amperes at 50 volts for five minutes. The product was partially fused but would not react with water, hot or cold.

As elementary phosphorus had been produced in large quantities, a test was made to see whether the product was simply oxide of magnesium or if it still contained pyrophosphate. A piece of the cake was dissolved in nitric acid, the magnesium was removed, and the filtrate gave a strong test for pyrophosphoric acid.

This showed that although considerable of the pyrophosphate had been reduced to elementary phosphorus, yet not all of it had acted in that manner. Therefore it seemed probable that more carbon was needed.

Consequently, in Run LXVIII, 40 grams more coke were added to this product and it was reheated for five minutes at 100 amperes and 50 volts. This gave negative results. Forty grams more coke were added and the mass reheated for five minutes at 200 amperes and 60 volts. This product also, would yield no phosphoretted hydrogen with water.

The question which now presented itself was, whether this result was due to employing a pyrophosphate, or whether magnesium phosphide could not be produced this way from any of its compounds.

To determine this, magnesium orthophosphate, $\text{Mg}_3\text{P}_2\text{O}_8$, was prepared. This does not change to pyrophosphate on heating.

The salt was prepared by precipitating magnesium chloride with Na_2HPO_4 .

In Run LXIX, 150 grams of the orthophosphate were mixed with 50 grams of coke and heated for six minutes at 150 amperes and 70 volts and then reheated for two minutes more at 175 amperes.

The product was not fused and would not evolve gas from either hot or cold water or dilute hydrochloric acid.

One great difference noted, however, was the absence of the elementary phosphorus which, when the pyrophosphate had been used, had been produced in such abundance.

A test of the product showed the absence of pyrophosphoric acid and the presence of an abundance of orthophosphoric acid, which demonstrated that little or no change had taken place in the charge.

In Run LXXI, in order to be sure whether reduction would or would not take place, a series of different strengths of current were tried. To avoid the mechanical loss of much of the charge, which in previous runs had passed out as fine dust, the charge was mixed to a thick paste with molasses.

The same proportions were kept as in Run LXIX and the charge was heated :

First : Five minutes with 100 amperes at 40 volts.

Second : Five minutes more with 100 amperes at 40 volts.

Third : Five minutes more with 150 amperes at 50 volts.

Fourth : Five minutes more with 225 amperes at 60 volts.

All of these gave negative results, thus showing that magnesium, either as pyro- or orthophosphate, is not thus reduced to the phosphide.

Note should also be made of the production of elementary phosphorus when the pyrophosphate is used and its absence when the orthophosphate is employed.

Magnesium having proved so entirely unsatisfactory for this purpose, a trial was made of the value of the phosphates of barium.

The orthophosphate was first prepared by precipitating from barium chloride with sodium hydrogen phosphate.

In Run LXX, 50 grams of this product were mixed with 50

grams of coke and heated for six minutes at 150 amperes and 60 volts, and then for two minutes more at 175 amperes and 65 volts. This product was well fused, and when placed in water evolved phosphoretted hydrogen most vigorously.

As a still further test regarding the use of pyrophosphates, barium pyrophosphate was made by precipitation from barium chloride with sodium pyrophosphate.

One hundred and fifty grams of this product were mixed with 50 grams of coke, and heated as before at 150 amperes and 60 volts for six minutes, and then for two minutes more at 175 amperes and 65 volts. This produced just the same sort of a product which, when placed in water, evolved gas with the greatest vigor.

A further investigation of this sort of reaction was made with ferric phosphate. This was prepared by precipitation from ferric chloride with disodium orthophosphate.

In Run LXXIII, 150 grams of this product were mixed with 50 grams of coke and heated for eight minutes at 175 amperes and 70 volts. Two small buttons of metallic appearance were the only parts of the product which were fused. These evolved hydrogen from dilute hydrochloric acid, but were unacted upon by water. The rest of the product would evolve no phosphoretted hydrogen. The buttons were evidently metallic iron.

As the metal is so easily reduced and as the phosphide does not stay in that condition even if it is formed, this preparation does not seem feasible.

This method then seems applicable to the alkaline earths only and phosphides of them may be produced from either ortho- or pyrophosphates. Neither magnesium phosphide nor the phosphides of metals easily reduced, may be obtained in this way.

When pyrophosphates are used, a considerable amount of elementary phosphorus is obtained. When orthophosphates are used this is unobserved.

PART IV.

Until the electric furnace made their formation comparatively easy, the borides were almost unknown, and even now

concerning many of them, there have not as yet been reports.

Moissan has made a few, notably, iron, cobalt, nickel, carbon, and lately of silicon.

So far as they have been investigated, the borides present definite formation and crystallization; they are stable and fuse at comparatively high temperatures.

From their high fusion-point, their hardness and good crystallization, it is quite possible that some of them may develop industrial uses.

The first of these made in this set of experiments was that of zirconium, on the formation of which no data whatever could be found.

The two available processes for the production of borides are either heating together the two elements in an electric furnace, or by passing chloride of boron over the metallic element. The former of these was selected as being the most practicable.

The zirconium salt available happened to be a nitrate. In order to reduce this to the elementary state, two processes were tried. First, the nitrate was ignited until it was all converted to the oxide. This was then subjected to the regular Goldsmith process, in which powdered aluminium was used, and the outside heat obtained from a gas furnace. The method did not prove satisfactory, and the reduced metal could not be well separated from the oxide of aluminium, which was doubtless crystallized by the intense heat.

Second, the nitrate was dissolved in cold water and the hydrate of zirconium precipitated from this by caustic soda. To prevent the hydrate from becoming insoluble, the precipitate was washed in cold water, and after washing it was dissolved in hydrofluoric acid, forming $\text{ZrF}_4 + 3\text{H}_2\text{O}$.

To this solution an excess of neutral potassium fluoride was added. This precipitated the basic salt potassium fluor-zirconate, the symbol of which is $3\text{KF} \cdot \text{ZrF}_4$.

After being dried, this potassium fluorzirconate was mixed in the proportion of one part to one and a half parts of powdered aluminium, placed in a graphite crucible and heated for one hour at the highest temperature of a blast-

furnace. The cake thus formed was boiled for three days with concentrated hydrochloric acid. Short of that time, even with suction on an asbestos filter, it was impossible to filter the mixture. After washing with hot water, the filtered residue was ready for use.

The elementary boron was prepared by a no less laborious process. Boric acid was fused, giving the anhydride. This was powdered and three parts of the anhydride were well mixed with one part of powdered magnesium. This mixture was heated for five minutes in a Hessian crucible placed in a gas furnace.

To remove magnesium borate, unchanged magnesium, etc., the cooled mass was boiled for three hours with water acidified with hydrochloric acid. The residue was filtered and washed and then treated for three days with boiling hydrochloric acid (sp. gr. 1.2).

This was then filtered, washed with water, then washed with alcoholic potash and then boiled for several hours with hydrofluoric acid. After final washing it was dried.

In Run LXXIV, having thus prepared these two elements, 15 grams of the zirconium were mixed with 2.2 grams of the boron, and the whole heated for five minutes in a carbon (not graphite) crucible at 200 amperes and 65 volts.

The product was a button, blackish on the outside, brittle, and on fracture of a steel-gray color. Under the microscope this proved to be of a distinctly crystalline structure. The formation was an agglomeration of brilliant, tabular, translucent to transparent crystals many being water-white.

The substance had a specific gravity of 3.7, and a hardness of 8.

It was slowly attacked by hot concentrated nitric acid and also by hot concentrated hydrochloric acid. Hot aqua regia reacted upon it vigorously, but none of them completely dissolved it.

Boiling liquid bromine gives no visible reaction with it, but it evidently attacked it somewhat as a test for zirconium was obtained with the solution.

Analyses of this compound were made, the boric acid was

treated according to the method of Gooch,¹ with methyl alcohol, and the zirconium was determined as oxide.

The amount of zirconium contained in the sample was found to be 86 per cent., which corresponds very closely with the theoretical content of zirconium in a boride where zirconium has a valence of four.

Therefore, the formula of this compound is undoubtedly Zr_3B_4 .

In Run LXXV, an attempt was made to produce a boride of bismuth. The charge was made up of 2.5 grams of powdered bismuth and 0.15 gram of elementary boron. This was heated for five minutes at 175 amperes and 60 volts; this produced simply a metallic button covered with unchanged boron.

Consequently the mass was reheated for five minutes at 225 amperes and 70 volts. The result of this was to produce a small amount of blackish crystalline substance which was acted upon slowly by hydrochloric and nitric acids and actively by hot aqua regia. Under the microscope the mass looked like graphite, but there had evidently been no combination.

In Run LXXVI, the same charge was subjected to 200 amperes and 75 volts for twelve minutes. As a result of this, practically nothing but some loose powder was left in the crucible. This, made it evident that before reaching a temperature sufficiently high to cause a combination of boron and bismuth, the latter is completely volatilized.

In Run LXXVII, another member of this same group of metals was tried. Here, an attempt was made to produce copper boride. The charge was made up of 7.5 grams of copper and 0.87 gram of boron. This was heated for five minutes, using 150 amperes and 60 volts.

This produced negative results and so the mixture was reheated for twelve minutes at 175 amperes and 65 volts. This product proved to be nothing but globules of copper and responded to all tests for the pure metal and none for a boride.

It, therefore, seemed that members of the copper group had

¹ Am. Chem. Jour., 9, 1887, p. 23.

no great tendency to combine with boron so a return was made to members and allied members of the iron group.

In Run LXXVIII, an investigation of the affinity of chromium for boron was made. A charge, consisting of 10 grams of metallic chromium and 2.1 grams of boron, was heated for six minutes at 175 amperes and 60 volts.

The product was a well-formed button greenish on the outside surface and of grayish metallic luster on fracture.

It had a specific gravity of 5. It was weakly attacked by nitric and hydrochloric acids and slowly by aqua regia. It was unaltered by standing in the air. It had a hardness of 8, was distinctly crystalline and had a conchoidal fracture.

In Run LXXIX, Run LXXVIII was repeated except that the boron was added in the amount of 2.5 grams and the amperage was raised to 200 and the voltage to 75. This heat was continued for ten minutes. The excess of boron was left unchanged and the product presented the same appearance and possessed the same properties as that obtained in the previous preparation.

Analyses of both of the products were made determining the chromium as oxide and treating the boron as before described. The results showed 82 per cent. of chromium which indicates CrB as the probable formula of the compound.

As tungsten is closely related to chromium it was selected as a promising element and a trial was made of its affinity for boron.

The metal tungsten may be prepared from alkali tungstates by acidifying their solutions with hydrochloric acid. This causes the precipitation of the trioxide, WO_3 . After being dried this can be reduced in the furnace. The charge used was in the proportion of ten parts tungsten trioxide to one part of carbon.

In Run LXXXI, for the preparation of the boride, 4 grams of tungsten were mixed with 0.2 gram of boron and then heated for five minutes at 175 amperes and 65 volts. This produced a good fusion and the product was silvery and metallic on fracture. It was very brittle and under the microscope showed octahedra in perfect crystallization.

Its hardness was 8 and its specific gravity was 9.6.

It was slowly acted upon by hot concentrated acids and hot *aqua regia* attacked it vigorously, forming the yellow trioxide.

An analysis was made of the product, calculating the tungsten as trioxide. The figures obtained showed the presence of 89 per cent. of metallic tungsten. This indicated the formula of WB_2 .

The final compound prepared was a boride of molybdenum. This was selected, as the element is closely related to chromium and tungsten, and the metal is rather easily prepared.

In Run LXXXII, the molybdenum was prepared from a charge of 120 grams of MoO_3 and 30 grams of coke. Here the heat was continued at 150 amperes and 50 volts.

In Run LXXXIII, since the former yield had been so small, the charge was changed to 300 grams of MoO_3 and 30 grams of coke. This was heated for twenty-five minutes at 200 amperes and 65 volts. This gave a good yield.

In Run LXXXIV, six grams of the metal thus prepared were mixed with one gram of boron and the whole heated for ten minutes at 200 amperes and 65 volts. As this caused no fusion, it was reheated for twelve minutes at 230 amperes and 70 volts.

This gave a good homogeneous button with a hardness of 9. It was quite brittle and, on fracture, showed brilliant metallic luster of pale brass color. It was crystalline in structure. Its specific gravity was found to be 7.105.

The substance was found to be very slowly attacked by cold acids with action increased by heating. It was attacked vigorously by *aqua regia*.

An analysis of the product, where the molybdenum was determined as lead molybdate, showed the presence of 86 per cent. of molybdenum which proves the formula of the boride to be Mo_3B_4 .

It has, therefore, been shown that boron does not readily combine with the members of the copper group and that it does have affinity for members and allied members of the iron group. On account of this latter fact, it was possible to pro-

duce four hitherto undetermined compounds; *viz.*, the borides of zirconium, chromium, tungsten, and molybdenum. The formula of these are respectively Zr_3B_4 , CrB , WB_2 , and Mo_3B_4 .

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